Metal-organic framework materials for hydrogen storage in aerospace applications

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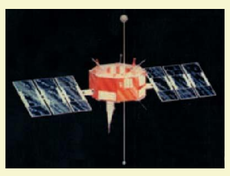
1. Hydrogen in aerospace applications

Timeline of hydrogen (H_2) within aerospace:

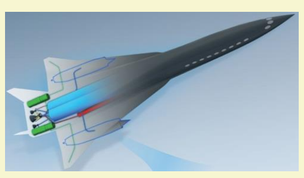
1783 – First hydrogen balloon flight

1954– Hydrogen peroxide Sikorsky Helicopter



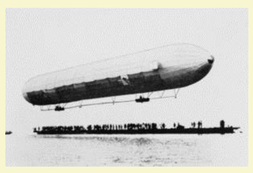
1966 – Hydrogen batteries in satellite (NTS-2)

1988– First hydrogen aircraft prototype (Tupolev Tu-155)

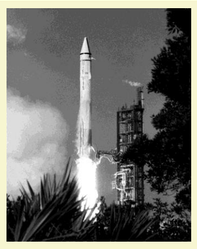


C21st – EADS 'ZEHST' – High speed transport concept study

1900 – First airship flown purely on hydrogen (Zeppelin LZ1)



1966 – Hydrogen used as a rocket fuel (Atlas-centaur launch vehicles)



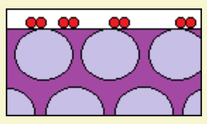
1969 – Hydrogen cryocooler on Mariner 6

2011 - Lange Aviation/DLR Antares H3 – hydrogen fuel cells (piloted and unmanned), 6000 km, >50 hrs[1]

Conventional storage methods: Compression or liquefaction.

Problem: Low H_2 densities and high investment costs.

Possible Solution: **Physisorption onto a porous material.**



BUT: Each additional kg sent into space costs ~ $ thousands!

2. Materials

Desired properties of solid adsorbent:

- ***Light***
- ***High surface area***
- ***Robust***
- ***Large pore volume***
- ***Low cost***
- ***Good cycle life***

➢ Metal-organic framework (MOF) chosen for study:

NH_2-MIL-101(Al)

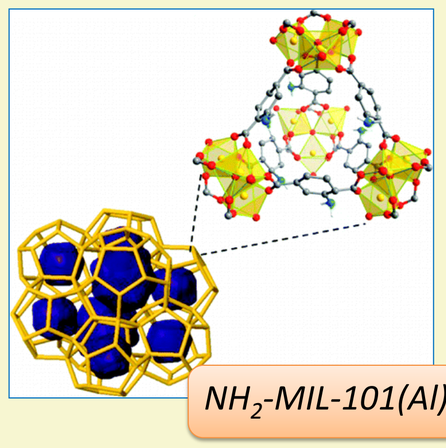
[SBU*: 634.04 g mol^{-1}]

c.f. heavier analogue [1]:

NH_2-MIL-101(Cr)

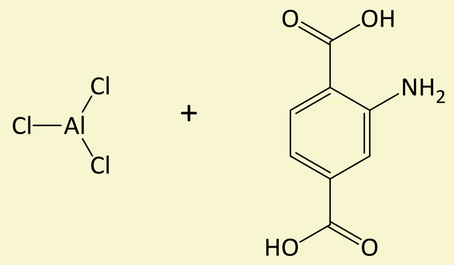
[SBU*: 712.37 g mol^{-1}]

(*Secondary Building Unit)



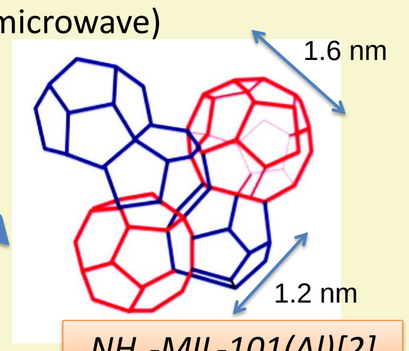
NH_2-MIL-101(Al) [2]

Synthesis of NH_2-MIL-101(Al) [2]

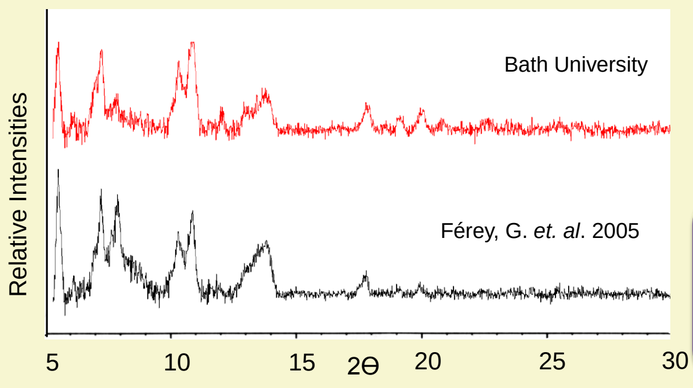


aluminum trichloride — 2-aminoterephthalic acid

Dimethylformamide (DMF)
130 °C
3 hours (microwave)

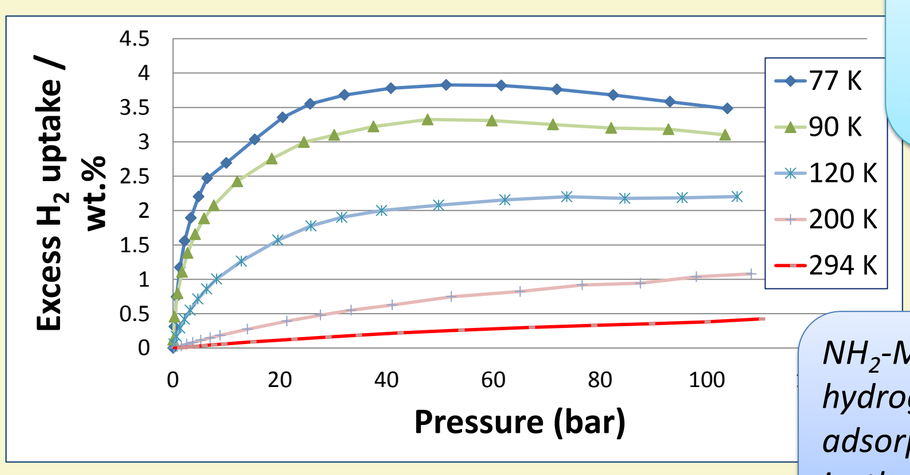


NH_2-MIL-101(Al)[2]



Comparison of powder XRD spectra for NH_2-MIL-101(Al) received in Bath and in literature [3]

3. Characterization of the MOF



D-R micropore volume NH_2-MIL-101(Al) [2]: 0.77 cm^3 g^{-1}

NH_2-MIL-101(Al) hydrogen excess adsorption isotherms

➢ Comparison of analogues

BET surface areas:

NH_2-MIL-101(Al) : 2540 m^2 g^{-1}

NH_2-MIL-101(Cr) : 1298 m^2 g^{-1}

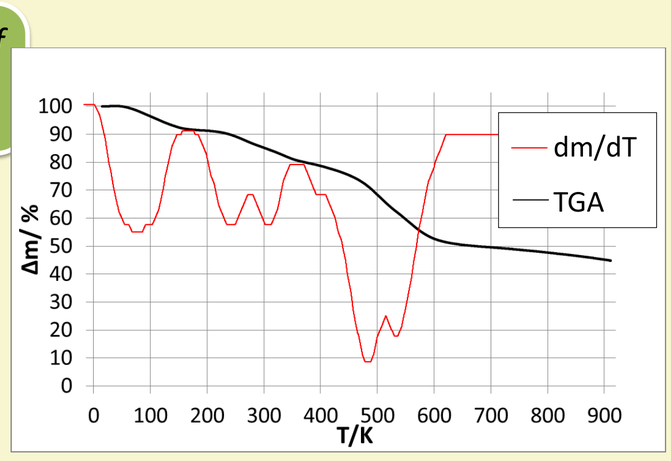
Max. hydrogen uptake at 77 K:

NH_2-MIL-101(Al) : 3.82 wt%

NH_2-MIL-101(Cr) : 2.66 wt%

Thermogravimetric analysis of NH_2-MIL-101(Al) (ramp rate - 5 °C min^{-1})

- Indicates guest solvent removal between 80-200 °C.
- Reveals interesting thermal degradation steps.

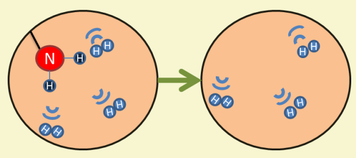


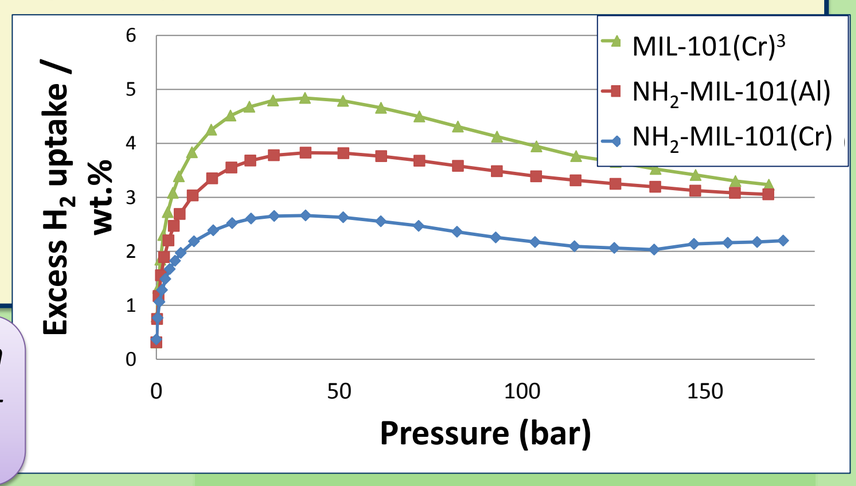
4. Ongoing work

D-R micropore volume MIL-101(Cr) [3]: 1.61 cm^3 g^{-1}

As seen in the figure below:

- Lighter analogue shows increased H_2 uptake.
- Removal of amine from NH_2-MIL-101(Cr) increases H_2 uptake.
- Potential for even higher uptake from removal of amine from NH_2-MIL-101(Al)?





Comparison of hydrogen excess isotherms for MIL-101 analogues at 77 K

5. Summary

- NH_2-MIL-101(Al) has greater BET surface area and H_2 uptake than the heavier Cr analogue.
- Removal of the NH_2 group from NH_2-MIL-101(Al) may result in very promising hydrogen uptake.
- Good initial results, but more materials need to be studied for potential commercial use.

1. JIANG, D., 2012. *Personal communication*, University of Bath.
2. SERRA-CRESPO, P., RAMOS-FERNANDEZ, E. V., GASCON, J. & KAPTEIJN, F. 2011. *Chemistry of Materials,* 23**,** 2565-2572.
3. FÉREY, G., MELLOT-DRAZNIEKS, C., SERRE, C., MILLANGE, F., DUTOUR, J., SURBLÉ & MARGIOLAKI. 2005. *Science 309 (5743), 2040-2042.*

Centre for Sustainable Chemical Technologies

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